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(54) FUEL CELL

(57)Abstract:

**PURPOSE:** To suppress a drop in catalyst utilization on discharge to enhance the cell performance of a polymer electrolyte fuel cell with a thin electrode catalyst layer comprising an electrolyte and catalyst-supporting carbon.

**CONSTITUTION:** A fuel cell consists of an electrolyte film made of a solid polymer, a fuel electrode and an air electrode placed on both sides of the electrolyte film, and the fuel electrode and the air electrode have a catalyst layer arranged so as to come in contact with the electrolyte film surface respectively. The catalyst layer is fabricated with carbon particles, a solid electrolyte, and a metallic catalyst which is supported on the carbon particle. The composite ratio of the metallic catalyst and the electrolyte in the catalyst layer to the carbon particles, which form an opposite side portion to the electrolyte film, of the electrolyte film is larger than the composite ratio of the metallic catalyst and the electrolyte in the catalyst layer to the carbon particles, which form an electrolyte side portion, of the electrolyte film.

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(54) 【発明の名称】 燃料電池

(57) 【要約】

【目的】 電解質と触媒担持炭素とから構成される薄い電極触媒層を有する高分子電解質型燃料電池の放電時の触媒利用率の低下を抑えて電池性能を向上させることを目的とする。

【構成】 固体高分子よりなる電解質膜と該電解質膜の両側に配置した燃料極と空気極とよりなり、該燃料極および空気極は、該電解質膜面に面接して配置された触媒層をもつ燃料電池において、上記触媒層は、炭素粒子と固体電解質と該炭素粒子に担持された触媒金属とで構成され、該触媒層の上記電解質膜とは反対側の部分を形成する該炭素粒子に対する該触媒金属および該触媒層中の電解質の配合割合は該触媒層の上記電解質側の部分を形成する該炭素粒子に対する該触媒金属および該触媒層中の電解質の配合割合より大きいことを特徴とする燃料電池。

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## 【特許請求の範囲】

【請求項 1】 固体高分子よりなる電解質膜と該電解質膜の両側に配置した燃料極と空気極とより、該燃料極および該空気極は、該電解質膜面に面接して配置された触媒層をもつ燃料電池において、上記触媒層は、炭素粒子と該炭素粒子に担持された触媒金属と電解質とで構成され、該触媒層の上記電解質膜とは反対側の部分を形成する該炭素粒子に対する該触媒金属および該触媒層中の電解質の配合割合は該触媒層の上記電解質膜側の部分を形成する該炭素粒子に対する該触媒金属および該触媒層中の電解質の配合割合より大きいことを特徴とする燃料電池。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、水素を含む燃料ガスおよび酸素を含有するガスより電気を発生させる燃料電池に関するものである。

## 【0002】

【従来の技術】 高分子電解質型燃料電池は、通常、加湿した固体高分子よりなる電解質膜とこの電解質膜を挟んで設けられた燃料極と空気極とで構成されている。この燃料極および空気極は、燃料ガスおよび空気などの酸素を含有するガスをそれぞれ電極反応を行わせる触媒層と燃料ガスおよび空気などの酸素を含有するガスの触媒層への供給路ならびに集電体として機能するガス拡散層との 2 層構造となっている。燃料ガスから触媒層での電極反応で形成された水素イオンが電解質内を移動し空気極側の触媒による電極反応で水となることで電流が出力される。（以下、単に「電解質」とは電解質膜と触媒層中の電解質との双方を言い、「電解質膜」、「触媒層中の電解質」とは区別する。）

上記の典型的な触媒層膜は、触媒（Pt 等）を高分散担持した炭素粒子（カーボンブラック）に疎水性バインダー粒子（フッ素樹脂粉末）を添加し、焼成成形により製造される。この触媒は比較的厚い（ $100\mu\text{m}$  以上）触媒層内に分散して存在しており、触媒表面への反応ガスの供給は疎水性粒子で形成された孔隙で確保されるものの、触媒と電解質との接触界面については触媒層形成時にはほとんど考慮されていない。

【0003】 上記の触媒層は電解質にホットプレスなどにより接合しただけではその界面での電気抵抗が大きく電流量の増大に伴う性能低下が大きい。そこで、電解質膜と触媒層とを接合する前に高分子電解質を溶解した溶液を触媒層に塗布して接合するなどの改善策が考案されている（J. Power Source, 22, 359 (1988)）。しかし、触媒担持炭素粒子とフッ素樹脂粉末との混合物からなる従来の触媒層は、通気性と強度を確保する関係上、厚さ約  $100\mu\text{m}$  以下とすることが困難であり、この厚さの触媒層全体に電解質を塗布して触媒と触媒層中の電解質との間の界面を形成することは

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事実上困難である。このため、電解質を塗布した電極より製作した電池でも触媒の利用率は一般に低く、高電流域で電池性能が低下し易いという問題がある。また、厚い触媒層の孔隙内にある触媒表面に触媒層中の電解質の塗布膜をガス拡散特性を損なわない程度に薄く形成するのは容易な技術ではない。したがって、従来の触媒層に電解質を塗布し低濃度分極も大きく高性能な電池を作製することは容易ではない。

【0004】 この従来電極の欠点を考慮して、最近全く新しいタイプの触媒層が考案されている。すなわち、この触媒層はフッ素樹脂粒子のような疎水化剤を全く含ない触媒層中の電解質と触媒を担持炭素のみからなる触媒層であり、電解質溶液と触媒担持炭素とを混練してから溶媒を蒸発させることにより形成される（J. Electrochem. Soc. Lett. L28 (1992), J. Appl. Electrochem. 22, 1 (1992)）。この触媒層では、触媒と触媒層中の電解質の配合比や成形条件の調節により触媒と電解質との界面の大きさおよび状態が制御可能になるとともに、約  $15\mu\text{m}$  以下の厚さまで薄くすることができる。このため、従来電池よりも高触媒利用率および低濃度分極の高性能電池が得られる。

【0005】 しかし、この触媒層の薄層化による上記の電池性能の向上は、触媒層の厚さが  $10\sim 15\mu\text{m}$  以下になるとその効果が小さくなる傾向があるという問題がある。これは触媒層での触媒担持炭素粒子間隙の大部分を埋める電解質相がほぼ唯一の水およびガスの輸送経路となる関係上、電極内で発生した液体水によるフラiddi ング現象が従来の触媒層より起こりやすいという性質があるからである。電流密度すなわち水発生速度が増加すると、冠水して電極反応に寄与しない触媒が増加することになり、失活する触媒の割合は触媒層が薄くなるほど高くなる。

【0006】 以上により、従来の電池では触媒層が液体水によるフラiddi ングが避けがたい現状では、触媒を均一に充填した層を単純に薄くするだけでは触媒金属の白金が有効に利用できず不経済であり、触媒と電解質との界面が大きい極薄触媒層の特徴を充分生かしていない。

## 【0007】

【発明が解決しようとする課題】 本発明は上記の事情に鑑みてなされたもので、電解質と触媒担持炭素とから構成される薄い電極触媒層を有する高分子電解質型燃料電池において、放電時の触媒利用率の低下を抑えて電池性能を向上させた燃料電池を提供することを目的とする。

## 【0008】

【課題を解決するための手段】 本発明の燃料電池は、固体高分子よりなる電解質膜と該電解質膜の両側に配置した燃料極と空気極とよりなり、該燃料極および該空気極は、該電解質膜面に面接して配置された触媒層をもつ燃

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料電池において、上記触媒層は、炭素粒子と固体電解質と該炭素粒子に担持された触媒金属とで構成され、該触媒層の上記電解質とは反対側の部分を形成する該炭素粒子に対する該触媒金属および該電解質の配合割合は該触媒層の上記電解質膜側の部分を形成する該炭素粒子に対する該触媒金属および該固体電解質の配合割合より大きいことを特徴とする。

【0009】本発明の燃料電池は、固体高分子よりなる電解質膜とこの電解質膜の両側に配置した燃料極と空気極とで構成され、空気極および燃料極はそれぞれ電解質の膜面に面接して配置された触媒層をもつものである。電解質膜は電荷担体 ( $H^+$ ) を透過させる電解質特性を示す高分子膜が使用できる。

【0010】空気極および燃料極には、電解質膜とは反対側の触媒層面にガス拡散層を配置してもよい。該ガス拡散層は、高いガス透過性および高電子伝導性を有する多孔質体で形成され、燃料ガス、空気などの酸素を含有するガスを触媒層に均一に供給する。ガス拡散層は通常炭素粒子と疎水性粒子との混合物を成形して作られる。

【0011】また、燃料極および空気極の他の構成要素である触媒層は炭素粒子とこの炭素粒子上に担持された触媒金属および電解質（触媒層中の電解質）とで構成されている。この触媒層を構成する炭素粒子は電子を運び、触媒層中の固体電解質は電荷担体である  $H^+$  を運ぶ。そして燃料極の触媒金属は水を  $H^+$  にし空気極の触媒金属は酸素と  $H^+$  とを反応させる。すなわち、触媒層は炭素粒子、触媒金属および触媒中の電解質の三者が共存し炭素粒子は触媒層を構成する主体となるもので、その存在量が多い。本発明にかかる触媒層では、炭素粒子表面に触媒金属が担持され、さらに触媒金属が担持された炭素粒子表面上を触媒層中の電解質が被覆する。炭素粒子上に分散担持された触媒粒子の全表面積のうち電解質と接触している部分の面積を触媒有効表面積と呼ぶことにする。この触媒有効表面積は電極反応に関与する触媒の最大表面積を示す。実際の電極反応に関与する触媒の表面積（たとえば、実効表面積と呼ぶことができる）は有効表面積よりも一般に小さく、その割合には反応ガスの触媒表面への拡散過程が関係する。具体的には触媒層の内部孔隙構造、反応生成水量および触媒金属を覆う電解質の厚さが反応ガスの拡散速度を左右する。触媒層が多孔であればある程、触媒金属を覆う電解質の厚さが薄い程実効表面積は触媒有効表面積に近くなる。

【0012】触媒の全表面積は、電解質を含まない触媒担持炭素粉末または成形体について、室温付近における  $CO$  の飽和化学（単分子）吸着量から計算するか、または透過型電子顕微鏡観察により測定した平均粒子径から求めることができる。通常、両者の方法で得られる結果は良く一致する。触媒有効表面積は、電気化学的方法

（電気二重層容量の水素吸着波成分測定、すなわち、触媒層に不活性ガス ( $N_2$ ) を供給し、電極電位 ( $v$  s,

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水素電極) を  $0.06 \sim 1.4$  V の範囲で反復掃引するサイクリックボルタムメトリー) により求めることができる。

【0013】本発明にかかる触媒層では、触媒層の電解質とは反対側（ガス拡散層がある場合にはガス拡散層側）の部分を形成する炭素粒子に対する触媒金属および触媒中の電解質の配合割合は触媒層の電解質側の部分を形成する炭素粒子に対する触媒金属および触媒中の電解質の配合割合より大きく傾斜配合されている。すなわち、触媒層の電解質膜とは反対側の部分の触媒有効表面積は触媒層の電解質膜側の部分の触媒有効表面積より大きい。

【0014】触媒層の厚さを導入される反応ガスの拡散の観点から見ると約  $10 \mu m$  以下とするのが好ましい。触媒層の厚さが増すほど、反応ガスの導入が困難となり実効表面積が小さくなる。そこで触媒層の厚さを約  $10 \mu m$  とし、低電流域の電池性能の点から触媒有効表面積を電極  $1 cm^2$  面積あたり  $400 cm^2$  程度に設定する。この条件では触媒層内の平均触媒有効表面積は触媒層  $1 cm^3$  あたり約  $40 cm^2$  以上必要となる。一方、触媒層を構成する触媒担持炭素粒子の担持量は触媒分散度の観点から炭素粒子と触媒金属の合計を  $100$  重量%（以下、%は特に断らないかぎり重量%を意味する。）とした場合、触媒金属は  $40\%$  以下とするのが望ましい。

【0015】触媒層の厚さ方向に触媒有効表面積の傾斜を設ける手段としては、次の方法を採用できる。具体的には、触媒担持量の異なる高分散触媒担持炭素粒子を数種類形成する。そして各種の炭素粒子し電解質を溶解した溶液とをそれぞれ混合する。これによりそれぞれ触媒有効表面積の異なる、触媒金属担持炭素粒子と電解質の溶液との混合ペーストが得られる。これらの溶液を触媒有効表面積の大きさの順に薄層を形成して積層することにより触媒有効表面積の傾斜をもつ触媒層を得ることができる。

【0016】なお、触媒を高濃度で担持すると炭素粒子うへの触媒の分散性を低下するので、何らかの高分散化対策を施すことが望ましい。たとえば、高表面積炭素担体（小粒径カーボンブラックなど）を使用する、熱酸化賦活法などにより炭素担体の表面積を拡大する、炭素担体表面の化学性状を修飾（硝酸酸化処理など）し炭素粒子への触媒または前駆体の吸着や濡れを促進する。触媒担持前または担持だんかでの第三成分添加などの対策である。

【0017】 $40\%$  の白金を担持した炭素粒子を電解質の溶液と混和して触媒層を形成すると、層内の触媒有効表面積は触媒層  $1 cm^3$  あたり約  $60 m^2$  となることがわかった。したがって、触媒有効表面積の傾斜を厚さ  $10 \mu m$  の触媒層内に直線的に設ける場合は、触媒層の一方の側端に約  $60 m^2$  の層を、逆の側端を約  $10 m^2$  の

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層としてその間に順に触媒有効表面積を減少させた層を重ねることにより形成できる。ちなみに、触媒を10%高分散担持した炭素粒子を電解質の溶液と混和して成形すると1cm<sup>3</sup>あたり約10m<sup>2</sup>の触媒有効表面積をもつ層が形成できる。

【0018】しかし、実際に触媒有効表面積にどのような傾斜を設けるかは、電極からの排水速度に影響する。ガス拡散層の性能および電池運転条件を考慮して決めるのが望ましい。触媒層内の反応ガスの濃度変化は、触媒層内での反応および拡散抵抗により、ガス拡散層側で濃度が高く、電解質膜側は低い傾向となるのが一般的である。また、電解質側はガス拡散を抑制する液体水の量も多い。してみると本発明にかかる触媒層は高電流密度域で反応ガス濃度が大きいところは単位体積あたりの触媒有効表面積を大きくし、反応ガス濃度が低下するところは逆に単位体積あたりの触媒有効表面積を小さくするような構成となっていることになる。

【0019】たとえば、空気極の触媒層では、ガスを触媒層に導入するガス拡散層に接触している側の触媒有効表面積を大きくし電解質膜側方向に向かって触媒有効表面積を小さくするような傾斜を設ける様に触媒有効表面積の異なるものを順次重ねて触媒層を形成する。これにより空気極では生成する液体水による影響を受ける触媒の量が少なくなるとともに、触媒層に導入される反応ガスとの電極反応を効率良く進行させることができる。このため高電流密度域での出力電圧の低下を最小限にすることができる。

【0020】

【作用】本発明の燃料電池では、触媒層内の触媒総量を変えことなく液体水の滞留が避けがたい部分の触媒量を減らすように触媒層内の触媒有効表面積が制御される。これにより、大部分の触媒が電極反応に寄与させることができる。すなわち、従来の燃料電池では低電流密度ではすべての触媒が反応に寄与するが、電流密度が増加してくると触媒層内の液体水が過剰となり触媒の利用率が一般に低下する。しかし、本発明によれば、触媒利用率低下を最小限に抑える構成としているため、低電流領域\*

6

\*の性能を変えことなく、高電流領域でも電極反応の低下を抑制して進行できる。このため広い電流範囲で高電圧の出力を保持することが可能となる。その結果、触媒利用率が向上し触媒の節約が可能となる。

【0021】特に空気極側では電解質膜側からガス拡散層側へ触媒有効表面積を増加させる構成とすることが有効である。

【0022】

【実施例】以下、実施例により具体的に説明する。

10 触媒層の作製

含浸法やコロイド分散法などにより表1に示すA、B、C、Dの4種の白金触媒の担持量が異なる白金担持炭素粉末を調製した。この4種の白金担持炭素粉末に表1に示す量の電解質（商品名NAFION）が溶解したアルコール溶液を混和し単位体積あたりの触媒有効表面積が異なる4種類の混合ペーストをほぼ同量ずつ調製した。

【0023】次にカーボン布に炭素粒子と疎水性粒子との混合物を塗布焼成した孔質体よりなる電極ガス拡散層を用意し、その片側に上記ペーストを触媒有効表面積の  
20 大きさの順（D←C←B←A）に塗布し層状に積層した。触媒有効表面積は電極単位面積当りDが98cm<sup>2</sup>、Cが79cm<sup>2</sup>、Bが46cm<sup>2</sup>、Aが27cm<sup>2</sup>でガス拡散層から順に小さくなっている。全体の触媒有効表面積は250cm<sup>2</sup>である。この積層の際、各層の界面部分のみが混じり合うように、各層形成時のペースト内溶媒（アルコールなど）の蒸発量を乾燥時間や外部条件（温度・雰囲気）などを調製した。

【0024】触媒層の形成作業は、はけ塗りなどの手作業でも可能であるが、スプレー法やスクリーン印刷ドクタープレート成形時などの方法でおこなうのが、均一性確保の点から望ましい。また触媒層の傾斜をより連続的に形成するには、触媒担持炭素粒子の比重差を利用した沈降転写法やペースト組成を連続的に変えながらスプレー塗布する方法が望ましい。

【0025】

【表1】

領域	A	B	C	D	全体
% Pt/C	10%	20%	30%	40%	—
Pt+C(mg)	0.40	0.30	0.40	0.45	1.55
Pt(mg)	0.04	0.06	0.12	0.18	0.40
電解質 (mg)	NAFION 0.02	各領域のPt/C 0.03	粉に溶液から添加混合 0.06	0.09	0.20
触媒層厚さ(μm)	2	2	2	2	8
Pt有効面(cm <sup>2</sup> )	27	46	79	98	250

(5)

最後に、電解質膜を別に作成した燃料極（触媒層は傾斜を設けないもの）と上記で作製した空気極（触媒層+ガス拡散層）の各々の触媒層側で挟み、プレス治具内に固定して30～150 kg/cm<sup>2</sup>の圧力をかけ、（この段階において電極触媒層内にはまだ少量の溶媒が残留していることが望ましい。）電解質膜の変質が起こらない範囲内で、できるだけ高い温度（120～150℃）で短時間（15分以内）ホットプレスして電池を作製した。

【0026】図1に上記方法で形成した空気極側の触媒層の積層状態の模式的に示す。

（比較例）比較例として表2に示す触媒層内にPtの有効表面積の傾斜を設けない4種の触媒層を用いた他は実施例と同じ電池を作製した。Ptの有効表面積は比較例\*

\*4を除いて実施例の250 cm<sup>2</sup>（全体）より大きくした。

【0027】この実施例と比較例1～4の5種の電池の常圧（H<sub>2</sub>/Air）70℃での電流密度と電池出力電圧との関係を調べた。結果を、図2に示す。比較例1～4では、電池性能がPt有効表面積よりもPt担持炭素量、すなわち、触媒層の厚さに支配されており、電流密度の増加により出力電圧の低下が比較例1→2→3→4の順で良くなっている。これは厚い触媒層ほどガス透過性が低下すること、触媒が液体水に陥没し失活しやすいことによる。

【0028】

【表2】

	Pt/C 粉(mg)	Pt(mg)	電解質(mg)	触媒層 厚さ μm	Pt有効表 面積 (cm <sup>2</sup> )
比較例 1	10%Pt/C(4.0)	0.4	NAFION(0.2)	24	270
比較例 2	20%Pt/C(2.0)	0.4	NAFION(0.2)	11	307
比較例 3	30%Pt/C(1.3)	0.4	NAFION(0.2)	6	262
比較例 4	40%Pt/C(1.0)	0.4	NAFION(0.2)	4	218

本実施例では触媒層は、全体で比較的高活性な比較例3とほぼ同等の厚さ（Pt/C量）および白金有効表面積をもつ。しかも、比較例と違って触媒層内のPt有効表面積の傾斜効果により、ガス濃度が高いところで反応が進行し触媒利用率が高く保持できるので、広い電流域で比較例4を上回る高い性能を示した。

【0029】

【発明の効果】本発明の触媒層の構成によれば、触媒利用率の高い反応ガス濃度の高い所に電解質と接触した触媒有効表面積を多くし、順次触媒有効表面積を低下させているので、電流密度が高くなる領域でも触媒利用率の

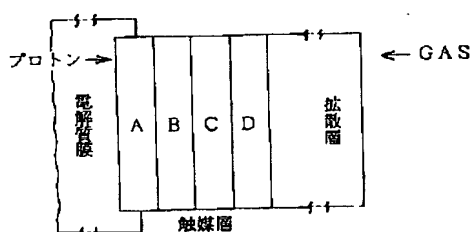
低下を最小限に抑えることができる。したがって、同一触媒量の従来電池に比べ、高電流密度における電池性能を著しく向上させることができる。また、この電池は触媒利用率が向上するので使用する触媒の節約が可能となる。

【図面の簡単な説明】

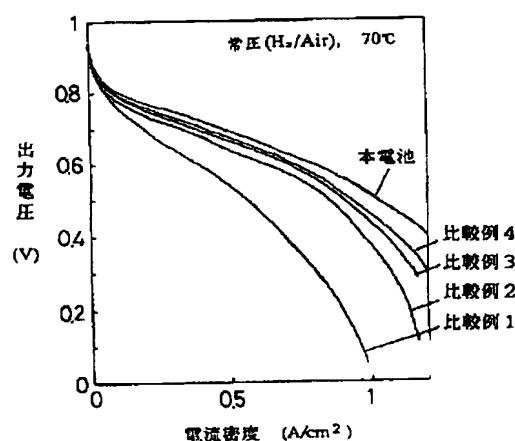
【図1】 この図は触媒有効表面積に傾斜を設けた本実施例の空気極側の触媒層（4領域分割した）の模式図である。

【図2】 この図は、電池の電池出力電圧と電流密度との関係を調べたグラフである。

【図1】



【図2】



(6)

フロントページの続き

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the fuel cell which generates the electrical and electric equipment from the gas containing the fuel gas and oxygen containing hydrogen.

[0002]

[Description of the Prior Art] The polyelectrolyte mold fuel cell consists of the fuel electrodes and air poles which were prepared on both sides of the electrolyte membrane which usually consists of a humidified solid-state macromolecule, and this electrolyte membrane. This fuel electrode and air pole have two-layer structure with the gaseous diffusion layer which functions as the supply way and charge collector to a catalyst bed of the gas containing oxygen, such as a catalyst bed to which electrode reaction is made to perform the gas containing oxygen, such as fuel gas and air, respectively, fuel gas, and air. A current is outputted by the hydrogen ion formed by the electrode reaction in a catalyst bed moving in the inside of an electrolyte, and becoming water from fuel gas by the electrode reaction by the catalyst by the side of an air pole. (Hereafter, an "electrolyte" only means the both sides of an electrolyte membrane and the electrolyte in a catalyst bed, and an "electrolyte membrane" and "the electrolyte in a catalyst bed" are distinguished.)

The above-mentioned typical catalyst bed film adds a hydrophobic binder particle (fluororesin powder) to the carbon particle (carbon black) which carried out high distribution support of the catalysts (Pt etc.), and is manufactured by baking shaping. This catalyst distributes and exists in a comparatively thick (100 micrometers or more) catalyst bed, and although supply of reactant gas on a catalyst front face is secured by the porous space formed by the hydrophobic particle, it is hardly taken into consideration about the contact interface of a catalyst and an electrolyte at the time of catalyst bed formation.

[0003] Only by joining to an electrolyte with a hotpress etc., the electric resistance in the interface is large, and the above-mentioned catalyst bed has the large degradation accompanying increase of the amount of currents. Then, before joining an electrolyte membrane and a catalyst bed, the remedy of applying to a catalyst bed the solution which dissolved the polyelectrolyte, and joining is devised (J. Power Source, 22,359 (1988)). However, on the relation which secures permeability and reinforcement, the conventional catalyst bed which consists of mixture of a catalyst support carbon particle and fluororesin powder is difficult to carry out to about 100 micrometers or less in thickness, and it is difficult the catalyst bed to apply an electrolyte to the whole catalyst bed of this thickness, and to form the interface between a catalyst and the electrolyte in a catalyst bed as a matter of fact. For this reason, there is a problem that the utilization factor of a catalyst is generally low and the cell engine performance tends to fall in a high current region also by the cell manufactured from the electrode which applied the electrolyte. Moreover, an easy technique does not form the spreading film of the electrolyte in a catalyst bed in the catalyst front face in the porous space of a thick catalyst bed thinly at extent which does not spoil a gaseous diffusion property. Therefore, it is not easy to apply an electrolyte to the conventional catalyst bed and for low concentration polarization to also produce a highly efficient large cell.

[0004] In consideration of the fault of an electrode, the catalyst bed new recently completely type is devised conventionally [ this ]. That is, after this catalyst bed is completely a catalyst bed which consists only of support carbon the electrolyte and catalyst in the catalyst bed which is not \*\* about a hydrophobing agent like a fluororesin particle and kneads an electrolytic solution and catalyst support carbon, it is formed by evaporating a solvent (22 J. Electrochem.Soc.Lett. L28 (1992), J.Appl.Electrochem. 1 (1992)). In this catalyst bed, while the magnitude and the condition of an interface of a catalyst and an electrolyte become controllable by the compounding ratio of the electrolyte in a catalyst and a catalyst bed, or accommodation of a process condition, it can be made thin to the thickness of about 15 micrometers or less. For this reason,

the high performance cell of a high catalyst utilization factor and low concentration polarization is conventionally obtained rather than a cell.

[0005] However, the improvement in the above-mentioned cell engine performance by the lamination of this catalyst bed has the problem that there is an inclination for that effectiveness to become small, when the thickness of a catalyst bed is set to 10-15 micrometers or less. This is because there is a property in which the flooding phenomenon by the liquid water generated on the relation in which the electrolyte phase which fills most catalyst support carbon particle gaps in a catalyst bed serves as the almost only water and a transportation path of gas, and within the electrode tends to happen from the conventional catalyst bed. If current density, i.e., a water generating rate, increases, the catalyst which is covered with water and does not contribute to electrode reaction will increase, and the rate of the deactivating catalyst will become so high that a catalyst bed becomes thin.

[0006] By the conventional cell, only by making thin simply the layer to which the catalyst bed filled up the catalyst into homogeneity with the present condition which flooding by liquid water cannot avoid easily, it cannot use effectively, and the platinum of a catalyst metal is uneconomical and cannot be utilizing thoroughly enough the description of an ultra-thin catalyst bed with the large interface of a catalyst and an electrolyte by the above.

[0007]

[Problem(s) to be Solved by the Invention] This invention was made in view of the above-mentioned situation, and aims at offering the fuel cell which suppressed decline in the catalyst utilization factor at the time of discharge, and raised the cell engine performance in the polyelectrolyte mold fuel cell which has the thin electrode catalyst bed which consists of an electrolyte and catalyst support carbon.

[0008]

[Means for Solving the Problem] The fuel cell of this invention consists of the fuel electrode and air pole which have been arranged on both sides of the electrolyte membrane which consists of a solid-state macromolecule, and this electrolyte membrane. This fuel electrode and this air pole In a fuel cell with the catalyst bed interviewed and arranged in this electrolyte membrane side the above-mentioned catalyst bed It consists of a carbon particle, a solid electrolyte, and a catalyst metal supported by this carbon particle. With the above-mentioned electrolyte of this catalyst bed, the blending ratio of coal of this catalyst metal to this carbon particle that forms the part of the opposite side, and this electrolyte is characterized by being larger than the blending ratio of coal of this catalyst metal to this carbon particle that forms the part by the side of the above-mentioned electrolyte membrane of this catalyst bed, and this solid electrolyte.

[0009] The fuel cell of this invention consists of the fuel electrodes and air poles which have been arranged on both sides of the electrolyte membrane which consists of a solid-state macromolecule, and this electrolyte membrane, and an air pole and a fuel electrode have the catalyst bed which interviewed the electrolytic film surface and has been arranged, respectively. An electrolyte membrane can use the poly membrane which shows the electrolyte property of making a charge carrier ( $H^+$ ) penetrating.

[0010] In an air pole and a fuel electrode, a gaseous diffusion layer may be arranged with an electrolyte membrane in the catalyst bed side of the opposite side. This gaseous diffusion layer is formed by the porous body which has high gas permeability and high electronic conduction nature, and supplies the gas containing oxygen, such as fuel gas and air, to a catalyst bed at homogeneity. A gaseous diffusion layer usually fabricates the mixture of a carbon particle and a hydrophobic particle, and is made.

[0011] Moreover, the catalyst bed which are other components of a fuel electrode and an air pole consists of the catalyst metals and electrolytes (electrolyte in a catalyst bed) which were supported on a carbon particle and this carbon particle. It is  $H^+$  whose solid electrolyte in a catalyst bed the carbon particle which constitutes this catalyst bed carries an electron, and is a charge carrier. It carries. And the catalyst metal of a fuel electrode is hydrogen  $H^+$  It carries out and the catalyst metal of an air pole is oxygen and  $H^+$ . It is made to react. That is, as for a catalyst bed, three persons of the electrolyte in a carbon particle, a catalyst metal, and a catalyst live together, a carbon particle serves as a subject who constitutes a catalyst bed, and there is much the abundance. The electrolyte in a catalyst bed covers with the catalyst bed concerning this invention the carbon particle front-face top where the catalyst metal was supported by the carbon particle front face, and the catalyst metal was supported further. The area of the part which touches the electrolyte among the total surface areas of the catalyst particle by which distributed support was carried out will be called a catalyst effective-surface product on a carbon particle. This catalyst effective-surface product shows the maximum surface area of the catalyst which can participate in electrode reaction. More generally than an effective-surface product the surface area (for example, it can be called effective surface area) of the catalyst which participates in actual electrode reaction is small, and the diffusion process on the front face of a

catalyst of reactant gas is related to the rate. Specifically, the thickness of a wrap electrolyte influences the diffusion rate of reactant gas for the internal pore structure, the amount of produced water, and catalyst metal of a catalyst bed. If a catalyst bed is porosity, effective surface area will become close to a catalyst effective-surface product about a catalyst metal a certain degree, so that the thickness of a wrap electrolyte is thin.

[0012] It can ask for the total surface area of a catalyst from the mean particle diameter which calculated about the catalyst support carbon powder or Plastic solid which does not contain an electrolyte from the saturation chemistry (single molecule) amount of adsorption of CO in near a room temperature, or was measured by transmission electron microscope observation. Usually, the result obtained by both approach is well in agreement. It can ask for a catalyst effective-surface product with an electrochemical process (cyclic voltammetry which supplies inert gas (N<sub>2</sub>) to hydrogen adsorption-wave component measurement of electric double layer capacity, i.e., a catalyst bed, and carries out the repetitive sweep of the electrode potential (vs, hydrogen electrode) in 0.06-1.4V).

[0013] In the catalyst bed concerning this invention, inclination combination of the blending ratio of coal of the electrolyte in the catalyst metal to the carbon particle which forms the part of the opposite side (gaseous diffusion layer side when there is a gaseous diffusion layer), and a catalyst is carried out with the electrolyte of a catalyst bed more greatly than the blending ratio of coal of the electrolyte in the catalyst metal to the carbon particle which forms the part by the side of the electrolyte of a catalyst bed, and a catalyst. That is, the electrolyte membrane of a catalyst bed of the catalyst effective-surface product of the part of the opposite side is larger than the catalyst effective-surface product of the part by the side of the electrolyte membrane of a catalyst bed.

[0014] When the thickness of a catalyst bed is seen from a viewpoint of diffusion of the reactant gas introduced, it is desirable to be referred to as about 10 micrometers or less. Installation of reactant gas becomes difficult and effective surface area becomes small, so that the thickness of a catalyst bed increases. Then, thickness of a catalyst bed is set to about 10 micrometers, and it is a catalyst effective-surface product 1cm of electrodes from the point of the cell engine performance of a low current region 2 It is 2 400cm per area. It is set as extent. At this condition, the average catalyst effective-surface product in a catalyst bed is 3 1cm of catalyst beds. It is 2 about 40cm of hits. It is above needed. On the other hand, when the amount of support of the catalyst support carbon particle which constitutes a catalyst bed makes the sum total of a carbon particle and a catalyst metal 100 % of the weight (especially % means weight % hereafter unless it refuses.) from a viewpoint of catalyst degree of dispersion, as for a catalyst metal, considering as 40% or less is desirable.

[0015] As a means to prepare the inclination of a catalyst effective-surface product in the thickness direction of a catalyst bed, the following approach is employable. Specifically, some kinds of high distribution catalyst support carbon particles from which the amount of catalyst support differs are formed. And the solution which various kinds carried out the carbon particle and dissolved the electrolyte is mixed, respectively. The mixed paste of the catalyst metal support carbon particle from which a catalyst effective-surface product differs by this, respectively, and an electrolytic solution is obtained. A catalyst bed with the inclination of a catalyst effective-surface product can be obtained by forming a thin layer and carrying out the laminating of these solutions in order of the magnitude of a catalyst effective-surface product.

[0016] in addition -- if a catalyst is supported with high concentration -- a carbon particle -- since the dispersibility of the upper catalyst is fallen, it is desirable to take a certain measures against high decentralization. For example, chemical property on the front face of a carbon carrier which uses high surface area carbon carriers (diameter carbon black of a granule etc.) and to which the surface area of a carbon carrier is expanded with a thermal oxidation activationsmethode etc. is embellished (oxidation-by-nitric-acid processing etc.), and it promotes adsorption of the catalyst to a carbon particle or a precursor, and \*\*\*\*. They are cures, such as third component addition before catalyst support or with a support \*\*\*\* paddle.

[0017] When it mixes with the carbon particle which supported 40% of platinum with an electrolytic solution and a catalyst bed is formed, the catalyst effective-surface product in a layer is 3 1cm of catalyst beds. It is 2 about 60m of hits. It turned out that it becomes. Therefore, when preparing the inclination of a catalyst effective-surface product linearly in a catalyst bed with a thickness of 10 micrometers, it is 2 about 60m to one side edge of a catalyst bed. It can form by piling up the layer as for which a reverse side edge is decreased in the meantime, and the layer decreased the catalyst effective-surface product in order as a layer of 2 by about 10m. When it mixes with the carbon particle which carried out quantity distribution support of the catalyst 10% with an electrolytic solution and it is incidentally fabricated, it is 3 1cm. It is 2 about 10m

of hits. A layer with a catalyst effective-surface product can be formed.

[0018] however, as for what kind of inclination is actually established in a catalyst effective-surface product, it is desirable to influence a wastewater rate from an electrode and to decide in consideration of the engine performance and cell service condition of a gaseous diffusion layer. As for concentration change of the reactant gas in a catalyst bed, it is common that concentration is high at a gaseous diffusion layer side, and an electrolyte membrane side serves as a low inclination by the reaction and diffused resistor within a catalyst bed. Moreover, an electrolyte side also has many amounts of the liquid water which controls gaseous diffusion. Then, as for the catalyst bed concerning this invention, the place where reactant gas concentration is large will enlarge catalyst effective area per unit volume in a high current density region, and the place to which reactant gas concentration falls will have composition which makes small conversely catalyst effective area per unit volume.

[0019] For example, in the catalyst bed of an air pole, a catalyst bed is formed for that from which a catalyst effective-surface product differs so that an inclination which enlarges the catalyst effective-surface product of the side in contact with the gaseous diffusion layer which introduces gas into a catalyst bed, and makes a catalyst effective-surface product small toward an electrolyte membrane side direction may be prepared in piles one by one. Thereby by the air pole, electrode reaction with the reactant gas both introduced into a catalyst bed as if the amount of the catalyst influenced by the liquid water to generate decreases can be advanced efficiently. For this reason, the fall of the output voltage in a high current density region can be made into the minimum.

[0020]

[Function] The catalyst effective area in a catalyst bed is controlled by the fuel cell of this invention to reduce the amount of catalysts of the part which stagnation of liquid water cannot avoid easily, without changing the catalyst total amount in a catalyst bed. Thereby, most catalysts can make it contribute to electrode reaction. That is, although all catalysts contribute to a reaction by the low current consistency with the conventional fuel cell, if current density increases, the liquid water in a catalyst bed will become superfluous, and, generally the utilization factor of a catalyst will fall. However, without changing the engine performance of a low current field, since the catalyst utilization factor fall is considered as the configuration suppressed to the minimum according to this invention, also in a high current field, the fall of electrode reaction is controlled and it can go on. For this reason, it becomes possible to hold the output of the high voltage in the large current range. Consequently, a catalyst utilization factor improves and saving of a catalyst is attained.

[0021] It is effective to consider as the configuration which makes a catalyst effective-surface product especially increase from an electrolyte membrane side to a gaseous diffusion layer side by the air pole side.

[0022]

[Example] Hereafter, an example explains concretely.

The platinum support carbon powder with which the amounts of support of four sorts of platinum catalysts shown in Table 1 by the production sinking-in method, a colloidal dispersion method, etc. of a catalyst bed, A, B, C, and D, differ was prepared. Electrolyte of the amount shown in four sorts of these platinum support carbon powder in Table 1 (trade name NAFION) The mixed paste which is four kinds from which it mixes with the alcoholic dissolved solution, and the catalyst effective-surface product per unit volume differs was prepared mostly tales doses every.

[0023] Next, the electrode gaseous diffusion layer which becomes a carbon cloth from \*\*\*\*\* which carried out spreading baking of the mixture of a carbon particle and a hydrophobic particle was prepared, the above-mentioned paste was applied to the one side in order of the magnitude (D<-C<-B<-A) of a catalyst effective-surface product, and the laminating was carried out to the shape of a layer. For 2 and B, 2 and A are [ a catalyst effective-surface product / D / 2 and C ] 2 27cm 46cm 79cm 98cm per electrode unit area. It is small sequentially from the gaseous diffusion layer. the whole catalyst effective-surface product -- 250cm<sup>2</sup> it is . At the time of this laminating, the evaporation of the solvents in a paste at the time of class formation (alcohol etc.) was prepared for the drying time, external conditions (temperature and ambient atmosphere), etc. so that only the interface part of each class might be mixed.

[0024] Although handicraft, such as brushing, is also possible, as for formation of a catalyst bed, it is desirable from the point of homogeneous reservation to carry out by the approaches at a spray method, the time of screen-stencil doctor plate shaping, etc. Moreover, in order to form the inclination of a catalyst bed more nearly continuously, the approach of carrying out a spray coating cloth is desirable, changing continuously the sedimentation replica method and paste presentation using the specific gravity difference of a catalyst support carbon particle.

[0025]

[Table 1]

A field A B C D The whole										% Pt/C 10% 20%	
30% 40% - Pt+C (mg)	0.40	0.30	0.40	0.45	1.55	Pt (mg)	0.04	0.06	0.12	0.18	0.40
electrolyte NAFION Pt/C of each field	It is addition mixing from a solution to powder. (mg)										
0.030.06 0.09 0.20 Catalyst bed thickness 2 (micrometer)	2	2	2	2	8	Pt					

measuring area (cm<sup>2</sup>) 27 46 79 98 250 ----- Finally an electrolyte membrane is inserted by each catalyst bed side of the fuel electrode (that in which a catalyst bed does not establish an inclination) created independently, and the air pole (catalyst bed + gaseous diffusion layer) produced by the above. It fixes in a press fixture and the pressure of 30-150kg/cm<sup>2</sup> is put (it is desirable for the little solvent to still remain in an electrode catalyst bed in this phase.), Within limits to which deterioration of an electrolyte membrane does not take place, the short-time (less than 15 minutes) hotpress was carried out at the highest possible temperature (120-150 degrees C), and the cell was produced.

[0026] It is shown typically [ the laminating condition of the catalyst bed by the side of the air pole formed in drawing 1 by the above-mentioned approach ].

(Example of a comparison) Four sorts of catalyst beds which do not prepare the inclination of the effective-surface product of Pt in the catalyst bed shown in Table 2 as an example of a comparison were used, and also the same cell as an example was produced. The effective-surface product of Pt was made larger than 250cm<sup>2</sup> (whole) of an example except for the example 4 of a comparison.

[0027] The relation between 70 degrees C [ of ordinary pressure of five sorts of cells of this example and the examples 1-4 of a comparison ] (H<sub>2</sub> / Air) current density and cell output voltage was investigated. A result is shown in drawing 2 . In the examples 1-4 of a comparison, the cell engine performance is governed by Pt support carbon content, i.e., the thickness of a catalyst bed, rather than Pt effective-surface product, and the fall of output voltage is good by the increment in current density in order of the example 1->2->3->4 of a comparison. A thicker catalyst bed depends this on that gas permeability falls and a catalyst caving in in liquid water and it being easy to deactivate.

[0028]

[Table 2]

Catalyst bed Pt effective table Pt/C Powder (mg)	Pt (mg)	Electrolyte (mg)
thickness mum Area (cm <sup>2</sup> ) ----- Example 1 of a comparison 10%Pt/C (4.0) 0.4		
NAFION (0.2) 24 270 Example 2 of a comparison 20%Pt/C (2.0) 0.4 NAFION (0.2) 11 307		
Example 3 of a comparison 30%Pt/C (1.3) 0.4 NAFION (0.2) 6 262 Example 4 of a comparison 40%Pt/C (1.0) 0.4		
NAFION (0.2) 4218 ----- this example -- a catalyst bed -- the whole --		

comparatively -- high -- it has thickness (the amount of Pt/C) almost equivalent to the activity example 3 of a comparison, and a platinum effective-surface product. And since unlike the example of a comparison the reaction advanced in the place where gas concentration is high and the catalyst utilization factor held highly according to the gap tilt effect of Pt effective-surface product in a catalyst bed, the high engine performance which exceeds the example 4 of a comparison in a large current region was shown.

[0029]

[Effect of the Invention] Since according to the configuration of the catalyst bed of this invention the catalyst effective-surface product in contact with an electrolyte is made [ many ] and the catalyst effective-surface product is reduced to the place where reactant gas concentration with a high catalyst utilization factor is high one by one, decline in a catalyst utilization factor can be suppressed also in the field in which current density becomes high to the minimum. Therefore, compared with the conventional cell of the amount of the same catalysts, the cell engine performance in high current density can be raised remarkably. Moreover, saving of the catalyst used since a catalyst utilization factor improves of this cell is attained.

[Translation done.]

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CLAIMS

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[Claim(s)]

[Claim 1] From the fuel electrode and air pole which have been arranged on both sides of the electrolyte membrane which consists of a solid-state macromolecule, and this electrolyte membrane, this fuel electrode and this air pole \*\*\*\*\* interviewed and arranged in this electrolyte membrane side is also set to \*\*\*\*\* . The above-mentioned catalyst bed It consists of the catalyst metals and electrolytes which were supported by the carbon particle and this carbon particle. With the above-mentioned electrolyte membrane of this catalyst bed, the part of the opposite side The blending ratio of coal of the electrolyte in this catalyst metal to this carbon particle to form and this catalyst bed is a fuel cell characterized by being larger than the blending ratio of coal of the electrolyte in this catalyst metal to this carbon particle that forms the part by the side of the above-mentioned electrolyte membrane of this catalyst bed, and this catalyst bed.

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[Translation done.]

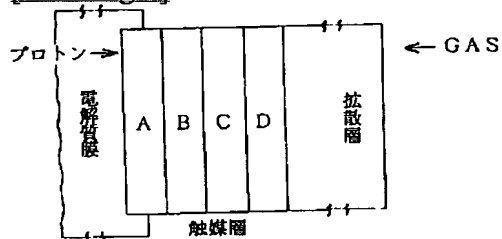
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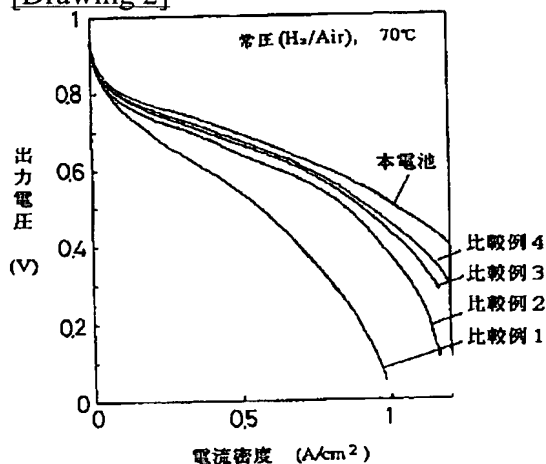
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## DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]

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